



## PHOSPHOR POWDERS AND METHOD FOR MAKING SAME

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### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates to phosphor powders and methods for producing  
5 phosphor powders. In particular, the present invention is directed to phosphor powders  
having small average particle size, a narrow particle size distribution, high crystallinity and  
spherical morphology. The present invention also relates to a method for continuously  
producing such powders and to devices that incorporate such powders.

#### 2. Description of Related Art

10 Phosphors are compounds that are capable of emitting useful quantities of radiation  
in the visible and/or ultraviolet spectrums upon excitation of the material by an external  
energy source. Due to this property, phosphor powders have long been utilized in cathode  
ray tube (CRT) screens for televisions and similar devices.

More recently, phosphor powders have been utilized in many advanced display  
15 devices that provide illuminated text, graphics or video output, including flat panel display  
devices such as liquid crystal displays, plasma displays, thick film and thin film  
electroluminescent displays and field emission displays.

Liquid crystal displays (LCD's) use a low power electric field to modify a light path and  
are commonly used in wristwatches, pocket televisions, gas pumps, pagers and the like.  
20 Plasma displays utilize a gas trapped between transparent layers that emits ultraviolet light  
when excited by a field. The ultraviolet light stimulates phosphors on the screen to emit  
visible light. Such plasma displays are used for large displays, such as at airport terminals.  
Thin film and thick film electroluminescent displays (TFEL's) utilize a film of phosphorescent  
material trapped between glass plates and electrodes to emit light in an electric field. Such  
25 displays are used in commercial transportation vehicles, factory floors and emergency

rooms. Field emission displays (FED's) are similar in principle to CRT's, wherein electrons emitted from a tip excite phosphors, which then emit light of different color.

Phosphor powders are also utilized in electroluminescent lamps (EL's), which include phosphor powder deposited on a polymer substrate which emits light when an electric field  
5 is applied.

There are a number of requirements for phosphor powders, which can vary dependent upon the specific application of the powder. Generally, phosphor powders should have one or more of the following properties: high purity; high crystallinity; small particle size; narrow particle size distribution; spherical morphology; controlled surface  
10 chemistry; homogenous distribution of the dopant; and good dispersibility. The proper combination of the foregoing properties will result in a phosphor with high luminescent intensity that can be used in many applications. It is also advantageous for many applications to provide phosphor powders that are coated, such as with a thin, uniform dielectric or semiconducting coating.

15 Numerous methods have been proposed for producing phosphor particles. One such method is referred to as the solid-state method. In this process, the phosphor precursor materials are mixed in the solid state and are heated so that the precursors react and form a powder of the phosphor material. For example, U.S. Patent No. 3,691,088 by Pelton discloses a process for making oxide-based phosphors by mixing precursor oxides with sulfur  
20 and heating the mixture in air for at least about 90 minutes. U.S. Patent No. 5,358,734 by Lenox et al. describes a process for producing a Ba-Mg-Al phosphor by forming a mixture of the oxides, halides and carbonates and firing the mixture in a reducing atmosphere. The powder is thereafter dry milled to reduce the particle size of the powder.

Solid-state routes, and many other production methods, utilize a grinding step to  
25 reduce the particle size of the powders. The mechanical grinding damages the surface of the phosphor, forming dead layers which inhibit the brightness of the phosphor powders.

Phosphor powders have also been made by liquid precipitation. In these methods, a solution which includes phosphor particle precursors is chemically treated to precipitate phosphor particles or phosphor particle precursors. These particles are typically calcined at an elevated temperature to produce the phosphor material. An example of this type of preparation is disclosed in U.S. Patent No. 5,413,736 by Nishisu et al. In yet another method, phosphor particle precursors or phosphor particles are dispersed in a solution which is then spray dried to evaporate liquid. The phosphor particles are thereafter sintered in the solid state at an elevated temperature to crystallize the powder and form a phosphor. Such a process is exemplified by U.S. Patent No. 4,948,527 by Ritsko et al. and U.S. Patent No. 3,709,826 by Pitt et al.

U.S. Patent No. 3,676,358 discloses a process wherein a solution of precursor nitrates are atomized and heated at 400°F to dry the particles. The particles are then reacted by passing the particles through a flame to form the phosphor.

Despite the foregoing, there remains a need for phosphor powders with high luminescent intensity that include particles having a substantially spherical morphology, narrow particle size distribution, a high degree of crystallinity and good homogeneity, which result in high luminescent intensity. The powder should have good dispersibility and the ability to be fabricated into thin layers having uniform thickness, resulting in a device with high brightness.

#### **SUMMARY OF THE INVENTION**

The present invention provides improved phosphor powder batches having a small particle size, narrow particle size distribution, spherical morphology and good crystallinity. The present invention also provides methods for forming such phosphor powder batches and devices incorporating such powder batches.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1-38 illustrate various embodiments of the method and apparatus of the present invention.

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## DESCRIPTION OF THE INVENTION

Referring now to Fig. 1, one embodiment of the process and apparatus of the present invention is described. A liquid feed 102 and a carrier gas 104 are fed to an aerosol generator 106 where an aerosol 108 is produced. The aerosol 108 is then fed to a furnace 110 where liquid in the aerosol 108 is removed to produce particles 112 that are dispersed in and  
10 suspended by gas exiting the furnace 110. The particles 112 are then collected in a particle collector 114 to produce a particulate product 116.

As used herein, the liquid feed 102 is a feed that includes one or more flowable liquids as the major constituent(s), so that the feed is flowable. The liquid feed 102 need not comprise only liquid constituents. The liquid feed 102 may comprise only liquid phase  
15 constituents, or it may also include particulate material suspended in a liquid phase. The liquid feed 102 must, however, be capable of being atomized to form droplets of sufficiently small size for preparation of the aerosol 108. Therefore, if the liquid feed 102 includes suspended particles, those particles should be micro-sized or nano-sized. Such suspended particles should typically be smaller than about 1 micron in size, preferably smaller than  
20 about 0.5 micron in size, and more preferably smaller than about 0.3 micron in size.

The liquid feed 102 includes at least one precursor material for preparation of the particles 112. The precursor material may be a substance in either a liquid or solid phase of the liquid feed 102. The precursor material may undergo one or more chemical reactions in the furnace 110 to assist in production of the particles 112. Alternatively, the precursor  
25 material may contribute to formation of the particles 112 without undergoing chemical reaction. This could be the case, for example, when the liquid feed 102 includes, as a

precursor material, suspended particles. The liquid feed 102 may include multiple precursor materials, which may be present together in a single phase or separately in multiple phases. For example, the liquid feed 102 may include multiple precursors in solution in a single liquid vehicle. Alternatively, one precursor material could be in a solid particulate phase and a  
5 second precursor material could be in a liquid phase. Also, one precursor material could be in one liquid phase and a second precursor material could be in a second liquid phase, such as could be the case for when the liquid feed 102 comprises an emulsion.

The carrier gas 104 may comprise any gaseous medium in which droplets produced from the liquid feed 102 may be dispersed in aerosol form. Also, the carrier gas 104 may be  
10 inert, in that the carrier gas 104 does not participate in formation of the particles 112. Alternatively, the carrier gas may have one or more active component(s) that contribute to formation of the particles 112. In that regard, the carrier gas may include one or more reactive components that react in the furnace 110 to contribute to formation of the particles 112. In many applications, air will be a satisfactory carrier gas, particularly when the  
15 particles 112 comprise oxide materials. In other instances, a relatively inert gas such as nitrogen may be required. This would sometimes be the case, for example, when preparing particles comprising sulfide materials or other materials that are free of oxygen.

The aerosol generator 106 must be capable of atomizing the liquid feed 102 to form droplets in a manner to permit the carrier gas 104 to sweep the droplets away to form the  
20 aerosol 108. The droplets comprise liquid from the liquid feed 102. The droplets may, however, also include nonliquid material, such as one or more small particles held in the droplet by the liquid. For example, when the particles 112 are composite particles, one phase of the composite may be provided in the liquid feed 102 in the form of suspended precursor particles and a second phase of the composite may be produced in the furnace  
25 110 from one or more precursors in the liquid phase of the liquid feed 102. Furthermore the precursor particles could be included in the liquid feed 102, and therefore also in droplets

of the aerosol 108, for the purpose only of dispersing the particles for subsequent compositional or structural modification during or after processing in the furnace 110 to remove liquid from the droplets.

The aerosol generator 106 is capable of producing the aerosol 108 such that it includes

5 droplets having a weight average size of smaller than about 20 microns, preferably smaller than about 10 microns, more preferably from about 1 micron to about 5 microns, and most preferably about 3 microns. The aerosol generator is also capable of producing the aerosol 108 such that it includes only droplets of a narrow size distribution. Preferably, the droplets in the aerosol are such that at least 70 percent (more preferably at least 80 weight percent

10 and most preferably at least 85 weight percent) of the droplets are smaller than about 20 microns, more preferably at least 70 weight percent (more preferably at least 80 weight percent and most preferably at least 85 weight percent) are smaller than about 10 microns, and even more preferably at least 70 weight percent (more preferably at least 80 weight percent and most preferably at least 85 weight percent) are smaller than about 5 microns.

15 Most preferably, at least 70 weight percent (more preferably at least 80 weight percent and most preferably at least 90 weight percent) of the droplets are of a size of from about 1 micron to about 5 microns.

The aerosol generator 106 is also capable of producing the aerosol 108 such that it has a high loading, or high concentration, of the liquid feed 102 in droplet form. In that regard,

20 the aerosol 108 preferably includes greater than about  $5 \times 10^6$  droplets per cubic centimeter of the aerosol 108, more preferably greater than about  $1 \times 10^7$  droplets per cubic centimeter of the aerosol 108 and most preferably greater than about  $5 \times 10^7$  droplets per cubic centimeter of the aerosol 108. That the aerosol generator 106 can produce such a heavily loaded aerosol 108 is particularly surprising considering the high quality of the aerosol 108

25 with respect to small droplet size and narrow droplet size distribution. When the aerosol 108 includes droplets of an average size of about 3 microns, for example, droplet loading in the

aerosol is such that the volumetric ratio of liquid feed 102 to carrier gas 104 in the aerosol 108 is typically larger than about 0.083 milliliters of liquid feed 102 per liter of carrier gas 102 in the aerosol 108, preferably larger than about 0.167 milliliters of liquid feed 102 per liter of carrier gas 104, and most preferably larger than about 0.333 milliliters of liquid feed 102 per liter of carrier gas 104. Stated another way, when average droplets in the aerosol 108 are about 3 microns in size, droplet loading in the aerosol 108 is such that the ratio of the rate of liquid feed 102 consumed in generating the aerosol 108 to the rate of carrier gas 104 consumed to generate the aerosol 108 is larger than about 5 milliliters per hour of liquid feed 102 per liter per minute of carrier gas 104, more preferably larger than about 10 milliliters per hour of liquid feed 102 per liter per minute of carrier gas 104, and most preferably larger than about 20 milliliters per hour of liquid feed 102 per liter per minute of carrier gas 104. This capability of the aerosol generator 106 to produce a heavily loaded aerosol 108 is even more surprising given the high droplet output rate of which the aerosol generator 106 is capable, as discussed more fully below. It will be appreciated that the concentration of liquid feed 102 in the aerosol 108 will depend upon the specific components and attributes of the liquid feed 102 and the size of the droplets produced in the aerosol 108. When reference is made to liters of carrier gas 104, it refers to the volume that the carrier gas 104 would occupy under conditions of standard transportation and pressure.

20 The furnace 110 may be any suitable device for heating the aerosol 108 to evaporate liquid from the droplets of the aerosol 108 and thereby permit formation of the particles 112. Typically, the furnace will be a tube furnace, so that the aerosol 108 moving into and through the furnace does not encounter sharp edges on which droplets could collect. Loss of droplets to collection at sharp surfaces results in lower yield of particles 112. More important, however, the accumulation of liquid at sharp edges can result in re-release of 25 undesirably large droplets back into the aerosol 108, which can cause contamination of the

particulate product 116 with undesirably large particles. Also, over time, such liquid collection at sharp surfaces can cause fouling of process equipment.

The particle collector 114, may be any suitable apparatus for collecting particles 112 to produce the particulate product 116. One preferred particle collector is a bag filter.

5        The process and apparatus of the present invention is well-suited for producing commercial-size batches of high quality particles of specialty materials. In that regard, the process and the accompanying apparatus provide versatility for preparing a wide variety of materials, and easily accommodate shifting of production between batches of different materials.

10        Of significant importance to the operation of the process of the present invention is the aerosol generator 106, which must be capable of producing a high quality aerosol with high droplet loading, as previously noted. With reference to Fig. 2, one embodiment of an aerosol generator 106 of the present invention is described. The aerosol generator 106 includes a plurality of ultrasonic transducer discs 120 that are each mounted in a transducer  
15        housing 122. The transducer housings 122 are mounted to a transducer mounting plate 124, creating an array of the ultrasonic transducer discs 120. The aerosol generator 106, as shown in Fig. 2, includes forty-nine transducers in a 7 x 7 array. The array configuration is as shown in Fig. 3, which depicts the locations of the transducer housings 122 mounted to the transducer mounting plate 124.

20        With continued reference to Fig. 2, a separation membrane 126, in spaced relation to the transducer discs 120, is retained between a bottom retaining plate 128 and a top retaining plate 130. Gas delivery tubes 132 are connected to gas distribution manifolds 134, which have gas delivery ports 136. The gas distribution manifolds 134 are housed within a generator body 138 that is covered by generator lid 140. A transducer driver 144, having  
25        circuiting for driving the transducer discs 120, is electronically connected with the transducer discs 120 via electrical cables 146.



During operation of the aerosol generator 106, as shown in Fig. 2, the transducer discs 120 are activated by the transducer driver 144 via the electrical cables 146. Liquid feed 102 enters through a feed inlet 148 and flows through flow channels 150 to exit through feed outlet 152. An ultrasonically transmissive fluid, typically water, enters through a water inlet 154 to fill a water bath volume 156 and flow through flow channels 158 to exit through a water outlet 160. A proper flow rate of the ultrasonically transmissive fluid is necessary to prevent overheating of the ultrasonically transmissive fluid. Ultrasonic signals from the transducer discs 120 are transmitted, via the ultrasonically transmissive fluid, across the water bath volume 156, and ultimately across the separation membrane 126 to the liquid feed 102 in flow channels 150. The ultrasonic signals from the ultrasonic transducer discs 120 cause atomization cones 162 to develop in the liquid feed 102 at locations corresponding with the transducer discs 120. Carrier gas 104 is introduced into the gas delivery tubes 132 and delivered to the vicinity of the atomization cones 162 via gas delivery ports 136. Carrier gas exits the gas delivery ports 136 in a direction so as to impinge on the atomization cones 162, thereby sweeping away atomized droplets of the liquid feed 102 that are being generated from the atomization cones 162 and creating the aerosol 108, which exits the aerosol generator 106 through an aerosol exit opening 164.

Efficient use of the carrier gas 104 is an important aspect of the aerosol generator 106 used with the process of the present invention. The embodiment of the aerosol generator 106 shown in Fig. 2 includes two gas exit ports per atomization cone, with the exiting carrier gas 104 being directed at the surface of the atomization cones 162, thereby efficiently distributing the carrier gas 104 to critical portions of the liquid feed 102 for effective and efficient sweeping away of droplets as they form about the atomization cones 162. The aerosol generator 106, therefore, permits generation of the aerosol 108 with heavy loading with droplets of the carrier liquid 102, unlike aerosol generator designs do not efficiently focus gas delivery to the locations of droplet formation.

Another important feature of the aerosol generator 106, as shown in Fig. 2, is the use of the separation membrane 126, which protects the transducers discs 120 from direct contact with the liquid feed 102, which is often highly corrosive. Although the aerosol generator 106 could be made without the separation membrane 126, in which case the liquid feed 102 would be in direct contact with the transducer discs 120, the highly corrosive nature of the liquid feed 102 can often cause premature failure of the transducer discs 120. The use of the separation membrane 126, in combination with use of the ultrasonically transmissive fluid in the water bath volume 56 to provide ultrasonic coupling, significantly extends the life of the ultrasonic transducers 120. One disadvantage of using the separation membrane 126, however, is that the rate of droplet production from the atomization cones 162 is reduced, often by a factor of two or more, relative to designs in which the liquid feed 102 is in direct contact with the ultrasonic transducer discs 102. Even with the separation membrane 126, however, the aerosol generator 106 used with the present invention is capable of producing a high quality aerosol with heavy droplet loading, as previously discussed. Suitable materials for the separation membrane 126 include, for example, polyamides (such as Capton™ membranes from DuPont) and other polymer materials, glass, and plexiglass. The main requirements for the separation membrane 126 are corrosion resistance and impermeability.

One alternative to using the separation membrane 126 is to bind a corrosion-resistant coating onto the surface of the ultrasonic transducer discs 120, thereby preventing the liquid feed 102 from contacting the surface of the ultrasonic transducer discs 120. Examples of such coating materials include platinum, Teflon, epoxies and various plastics. Although the coating does typically extend transducer life, after extended operation the coatings sometimes separate from the transducer surface, impairing transducer operation.

The design for the aerosol generator 106 based on an array of ultrasonic transducers is versatile and is easily modified to accommodate different generator sizes for different

applications. Figs. 4-15 show component designs for an aerosol generator 106 including an array of 400 transducers.

Referring first to Figs. 4 and 5, the transducer mounting plate 124 is shown with a design to accommodate an array of 400 ultrasonic transducers, arranged in four subarrays of 100 ultrasonic transducers each. The transducer mounting plate 124 has integral vertical walls 172 for containing the ultrasonically transmissive fluid, typically water, in a water bath similar to the water bath volume 156 described previously with reference to Fig. 2.

As shown in Figs. 4 and 5, four hundred transducer mounting receptacles 174 are provided in the transducer mounting plate 124 for mounting ultrasonic transducers for the desired array. With reference to Fig. 6, the profile of an individual transducer mounting receptacle 174 is shown. A mounting seat 176 accepts an ultrasonic transducer for mounting, with a mounted ultrasonic transducer being held in place via screw holes 178. Opposite the mounting receptacle 176 is a flared opening 180 through which an ultrasonic signal may be transmitted for the purpose of generating the aerosol 108, as previously described with reference to Fig. 2. With the mounting seats 176, it is not necessary to use the separate transducer housings 122 that were previously described with reference to the embodiment of the aerosol generator 106 shown in Fig. 2.

Referring now to Fig. 7, the bottom retaining plate 128 for a 400 transducer array is shown having a design for mating with the transducer mounting plate 124 (shown in Figs. 4-5). The bottom retaining plate 128 has eighty openings 184, arranged in four subgroups 186 of twenty openings 184 each. Each of the openings 184 corresponds with five of the transducer mounting receptacles 174 (shown in Figs. 4 and 5), when the bottom retaining plate 128 is mated with the transducer mounting plate 124 to create a volume for a water bath between the transducer mounting plate 124 and the bottom retaining plate 128. The openings 184, therefore, provide a pathway for ultrasonic signals generated by transducers to be transmitted through the bottom retaining plate.

Referring now to Figs. 8 and 9, a liquid feed box 190 for a 400 transducer array is shown having the top retaining plate 130 designed to fit over the bottom retaining plate 128 (shown in Fig. 7), with a membrane being retained between the bottom retaining plate 128 and the top retaining plate 130 when the aerosol generator 106 is assembled. The liquid feed box 190 also includes vertically extending walls 192 for containing liquid feed when the aerosol generator is in operation. Also shown in Figs. 8 and 9 is the feed inlet 148 and the feed outlet 152. An adjustable weir 198 determines the level of liquid feed 102 in the liquid feed box 190 during operation of the aerosol generator 106.

The top retaining plate 130 of the liquid feed box 190 has eighty openings 194 therethrough, which are arranged in four subgroups 196 of twenty openings 194 each. The openings 194 of the top retaining plate 130 correspond in size with the openings 184 of the bottom retaining plate 128 (shown in Fig. 7). When the aerosol generator 106 is assembled, the openings 196 through the top retaining plate 130 and the openings 184 through the bottom retaining plate 128 are aligned, with a membrane positioned therebetween, to permit transmission of ultrasonic signals when the aerosol generator 106 is in operation.

Referring now to Figs. 8-10, a plurality of gas tube feed-through holes 202 extend through the vertically extended walls 192 to either side of the assembly including the feed inlet 148 and feed outlet 152 of the liquid feed box 190. The gas tube feed-through holes 202 are designed to permit insertion therethrough of gas tubes 208 of a design as shown in Fig. 10. When the aerosol generator 106 is assembled, a gas tube 208 is inserted through each of the gas tube feed-through holes 202 so that gas delivery ports 136 in the gas tube 208 will be properly positioned and aligned adjacent the openings 194 in the top retaining plate 130 for delivery of gas to atomization cones that develop in the liquid feed box 190 during operation of the aerosol generator 106.

Referring now to Fig. 11 a partial view of the liquid feed box 190 is shown with gas tubes 208A, 208B and 208C positioned adjacent to the openings 194 through the top

retaining plate 130. Also shown in Fig. 11 are the relative locations that ultrasonic transducers 210 occupy when the aerosol generator 106 is assembled. As seen in Fig. 11, the gas tube 208A, which is at the edge of the array, has five gas delivery ports 136. Each of the gas delivery ports 136 is positioned to deliver carrier gas 104 to a different one of  
5 atomization cones that develop over the ultrasonic transducers 210 when the aerosol generator 106 is operating. The gas tube 208B, which is one row in from the edge of the array, is a shorter tube that has ten gas delivery ports 136, five each on opposing sides of the gas tube 208B. The gas tube 208B, therefore, has gas delivery ports 136 for delivering gas to atomization cones corresponding with each of ten ultrasonic transducers 210. The third gas  
10 tube, 208C, is a longer tube that also has ten gas delivery ports 136 for delivering gas to atomization cones corresponding with ten ultrasonic transducers 210. The design shown in Fig. 11, therefore, includes one gas delivery port per ultrasonic transducer 210. Although this is a lower density of gas delivery ports 136 than the embodiment shown in Fig. 2, which includes two gas delivery ports per transducer, the design shown in Fig. 11 is, nevertheless,  
15 capable of producing a dense, high-quality aerosol without unnecessary waste of gas.

Referring now to Figs. 12 and 13, a gas manifold 220 is shown for distributing gas to the gas tubes 208 in a 400 transducer array design. The gas manifold 220 includes a gas distribution box 222, and piping stubs 224 for connection with gas tubes 208 (shown in Fig. 10). Inside the gas distribution box 222 are two gas distribution plates 226 that form a flow  
20 path to assist in distributing the gas equally throughout the gas distribution box 222, to promote substantially equal delivery of gas through the piping stubs 224. The gas manifold 220, as shown in Figs. 12 and 13, is designed to feed eleven gas tubes 208. For the 400 transducer design, a total of four gas manifolds 220 are required.

Referring now to Figs. 14 and 15, the generator lid 140 is shown for a 400 transducer  
25 array design. The generator lid 140 mates with and covers the liquid feed box 190 (shown in Figs. 8 and 9). The generator lid 140, as shown in Figs. 14 and 15, has a hood design to

permit easy collection of the aerosol 108 without subjecting droplets in the aerosol 108 to sharp edges on which droplets may coalesce and be lost, and possibly interfere with the proper operation of the aerosol generator 106. When the aerosol generator 106 is in operation, the aerosol 108 would be withdrawn via the aerosol exit opening 164 through the  
5 generator cover 140.

Although the aerosol generator 106 produces a high quality aerosol 108 having a high droplet loading, it is often desirable to further concentrate the aerosol 108 prior to introduction into the furnace 110. Referring now to Fig. 16, a process flow diagram is shown for an one embodiment of the present invention involving such concentration of the aerosol  
10 108. As shown in Fig. 16, the aerosol 108 from the aerosol generator 106 is sent to an aerosol concentrator 236 where excess carrier gas 238 is withdrawn from the aerosol 108 to produce a concentrated aerosol 240, which is then fed to the furnace 110.

The aerosol concentrator 236 typically includes one or more virtual impactor capable of concentrating droplets in the aerosol 108 by a factor of greater than about 2, preferably  
15 by a factor of than about 5, and most preferably by a factor of greater than about 10, to produce the concentrated aerosol 240. According to the present invention, the concentrated aerosol 240 should typically contain greater than about  $1 \times 10^7$  droplets per cubic centimeter, and more preferably from about  $5 \times 10^7$  to about  $5 \times 10^8$  droplets per cubic centimeter. A concentration of about  $1 \times 10^8$  droplets per cubic centimeter of the  
20 concentrated aerosol is particularly preferred, because when the concentrated aerosol 240 is loaded more heavily than that, then the frequency of collisions between droplets becomes large enough to impair the properties of the concentrated aerosol 240, resulting in potential contamination of the particulate product 116 with an undesirably large quantity of oversized particles. For example, if the aerosol 108 has a concentration of about  $1 \times 10^7$  droplets  
25 per cubic centimeter, and the aerosol concentrator 236 concentrates droplets a factor of 10, then the concentrated aerosol 240 will have a concentration of about  $1 \times 8$  droplets per cubic

centimeter. Stated another way, for example, when the aerosol generator generates the aerosol 108 with average droplets of about three microns in size, the aerosol 108 with a droplet loading of about 0.167 milliliters liquid feed 102 per liter of carrier gas 104, the concentrated aerosol 240 would be loaded with about 1.67 milliliters of liquid feed 102 per  
5 liter of carrier gas 104. Stated as a ratio of the rate of liquid feed 102 in the aerosol 108 to the rate of carrier gas 104 in the aerosol 108, with an average droplet size of about three microns, and loading in the aerosol 108 of 10 milliliters per hour of liquid feed 102 per liter per minute of carrier gas 104, concentration by ten times would result in a concentrated aerosol 240 having a ratio of approximately 100 milliliters per hour of liquid feed 102 per liter  
10 per minute of carrier gas 104.

Having a high droplet loading in aerosol feed to the furnace provides the important advantage of reducing the heating demand on the furnace and the size of flow conduits required through the furnace. Concentration of the aerosol stream prior to entry into the furnace, therefore, provides a substantial advantage relative to processes that process  
15 leaner aerosol streams.

The excess carrier gas 238 that is removed in the aerosol concentrator 236 typically includes extremely small droplets that are also removed from the aerosol 108. For example, a virtual impactor sized to treat an aerosol stream having an average droplet size of about three microns might be designed to remove with the excess carrier gas 238 most droplets  
20 smaller than about 1 micron in size. Other designs are also possible. When using the aerosol generator 106 with the present invention, however, the loss of these very small droplets in the aerosol concentrator 236 will typically constitute no more than about ten percent by weight, and more preferably no more than about 5 percent by weight, of the droplets originally in the aerosol stream that is fed to the concentrator 236.

25 One embodiment of a virtual impactor that could be used as the aerosol concentrator 236 will now be described with reference to Figs. 17-23. A virtual impactor 246 includes an

upstream plate assembly 248 (details shown in Figs. 18-20) and a downstream plate assembly 250 (details shown in Figs. 21-23), with a concentrating chamber 262 located between the upstream plate assembly 248 and the downstream plate assembly 250.

Through the upstream plate assembly 248 are a plurality of vertically extending inlet  
5 slits 254. The downstream plate assembly 250 includes a plurality of vertically extending exit  
slits 256 that are in alignment with the inlet slits 254. The exit slits 254 are, however, slightly  
wider than the inlet slits 254. The downstream plate assembly 250 also includes flow channels  
258 that extend substantially across the width of the entire downstream plate assembly 250,  
with each flow channel 258 being adjacent to an excess gas withdrawal port 260.

10 During operation, the aerosol 108 passes through the inlet slits 254 and into the  
concentrating chamber 262. Excess carrier gas 238 is withdrawn from the concentrating  
chamber 262 via the excess gas withdrawal ports 260. The withdrawn excess carrier gas 238  
then exits via a gas duct port 264. That portion of the aerosol 108 that is not withdrawn  
through the excess gas withdrawal ports 260 passes through the exit slits 256 and the flow  
15 channels 258 to form the concentrated aerosol 240. Those droplets passing across the  
concentrating chamber 262 and through the exit slits 256 are those droplets of a large  
enough size to have sufficient momentum to resist being withdrawn with the excess carrier  
gas 238.

As seen best in Figs. 18-23, the inlet slits 254 of the upstream plate assembly 248  
20 include inlet nozzle extension portions 266 that extend outward from the plate surface 268  
of the upstream plate assembly 248. The exit slits 256 of the downstream plate assembly 250  
include exit nozzle extension portions 270 extending outward from a plate surface 272 of the  
downstream plate assembly 250. These nozzle extension portions 266 and 270 are important  
for operation of the virtual impactor 246, because having these nozzle extension portions  
25 266 and 270 permits a very close spacing to be attained between the inlet slits 254 and the  
exit slits 256 across the concentrating chamber 262, while also providing a relatively large



space in the concentrating chamber 262 to facilitate efficient removal of the excess carrier gas 238.

Also as best seen in Figs. 18-23, the inlet slits 254 have widths that flare outward toward the side of the upstream plate assembly 248 that is first encountered by the aerosol 108 during operation. This flared configuration reduces the sharpness of surfaces encountered by the aerosol 108, reducing the loss of aerosol droplets and potential interference from liquid buildup that could occur if sharp surfaces were present. Likewise, the exit slits 256 have a width that flares outward towards the flow channels 258, thereby allowing the concentrated aerosol 240 to expand into the flow channels 258 without encountering sharp edges that could cause problems.

As noted previously, both the inlet slits 254 of the upstream plate assembly 248 and the exit slits 256 of the downstream plate assembly 250 are vertically extending. This configuration is advantageous for permitting liquid that may collect around the inlet slits 254 and the exit slits 256 to drain away. The inlet slits 254 and the exit slits 256 need not, however, have a perfectly vertical orientation. Rather, it is often desirable to slant the slits backward (sloping upward and away in the direction of flow) by about five to ten degrees relative to vertical, to enhance draining of liquid off of the upstream plate assembly 248 and the downstream plate assembly 250. This drainage function of the vertically extending configuration of the inlet slits 254 and the outlet slits 256 also inhibits liquid build-up in the vicinity of the inlet slits 248 and the exit slits 250, which liquid build-up could result in the release of undesirably large droplets into the concentrated aerosol 240.

As discussed previously, the aerosol generator 106 of the present invention produces a concentrated, high quality aerosol of micro-sized droplets having a relatively narrow size distribution. It has been found, however, that for many applications the process of the present invention is significantly enhanced by further classifying by size the droplets in the aerosol 108 prior to introduction of the droplets into the furnace 110. In this manner, the

size and size distribution of particles in the particulate product 116 is further controlled.

Referring now to Fig. 24, a process flow diagram is shown for one embodiment of the process of the present invention including such droplet classification. As shown in Fig. 24, the aerosol 108 from the aerosol generator 106 goes to a droplet classifier 280 where  
5 oversized droplets are removed from the aerosol 108 to prepare a classified aerosol 282. Liquid 284 from the oversized droplets that are being removed is drained from the droplet classifier 280. This drained liquid 284 may advantageously be recycled for use in preparing additional liquid feed 102.

Although any suitable droplet classifier may be used for removing droplets above a  
10 predetermined size, a preferred droplet classifier is an impactor. One embodiment of an impactor for use with the present invention will be described with referenced Figs. 25-29.

As seen in Fig. 25, an impactor 288 has disposed in a flow conduit 286 two flow control plates 290, between which is located an impactor plate assembly 292. The flow control plates 290 are conveniently mounted on mounting plates 294. A drain 296 is located between the  
15 flow control plates 290.

The flow control plates 290 are used to channel the flow of the aerosol stream toward and away from the impactor plate assembly 292 in a manner with controlled flow characteristics that are desirable for proper impaction of oversize droplets on the impactor plate assembly 292 for removal through the drain 296. One embodiment of the flow control  
20 plate 290 is shown in Fig. 26. The flow control plate 290 has an array of circular flow ports 296 for channeling flow of the aerosol 108 towards the impactor plate assembly 292 and for channeling flow of the classified aerosol 282 away from the impactor plate assembly 292.

Details of the mounting plate 294 are shown in Fig. 27. The mounting plate 294 has a mounting flange 298 with a large diameter flow opening 300 passing therethrough to  
25 permit access of the aerosol 108 to the flow ports 296 of the flow control plate 290 (shown in Fig. 26).

Referring now to Figs. 28 and 29, one embodiment of an impactor plate assembly 292 is shown. The impactor plate assembly 292 includes an impactor plate 302 and mounting brackets 304 and 306 used to mount the impactor plate 302 inside of the flow conduit 286. The impactor plate 302 is sized and spaced a distance from the flow channel plates 290 so  
5 that droplets larger than a predetermined size will have a momentum that is too large for those particles to change flow direction to navigate around the impactor plate 302. Those large droplets will, therefore, impact on the impactor plate 302 and will drain down the impactor plate 302 to collect at the bottom of the conduit 286 and drain out of the drain 296.

10 During operation of the impactor 288, the aerosol 108 from the aerosol generator 106 passes through the upstream flow control plate 290. Most of the droplets in the aerosol navigate around the impactor plate 302 and exit the impactor 288 through the downstream flow control plate 290 in the classified aerosol 282. Droplets in the aerosol 108 that are too large to navigate around the impactor plate 302 will impact on the impactor plate 302 and  
15 drain through the drain 296 to be collected with the drained liquid 284 (as shown in Fig. 24).

The configuration of the impactor plate 302 shown in Fig. 28 represents only one of many possible configurations for the impactor plate 302. For example, the impactor 288 could include an upstream flow control plate 290 having vertically extending flow slits therethrough that are offset from vertically extending flow slits through the impactor plate  
20 302, such that droplets too large to navigate the change in flow due to the offset of the flow splits between the flow control plate 290 and the impactor plate 302 would impact on the impactor plate 302 to be drained away. Other designs are also possible.

In a preferred embodiment of the present invention, the droplet classifier 280 is typically designed to remove droplets from the aerosol 108 that are larger than about 10  
25 microns in size, more preferably to remove droplets of a size larger than about 8 microns in size and most preferably to remove droplets larger than about 5 microns in size. Depending

upon the specific application, however, the droplet size for removal may be varied by changing the spacing between the flow control plate 290 and the impactor plate 302 and by varying the configuration of the impactor plate 302. Because the aerosol generator 106 of the present invention initially produces a high quality aerosol 108, having a relatively narrow  
5 size distribution of droplets, typically less than about 25 weight percent of liquid feed 102 in the aerosol 108 is removed as the drain liquid 284 in the droplet classifier 288, with preferably less than about 20 weight percent being removed and most preferably less than about 15 weight percent being removed. Minimizing the removal of liquid feed 102 from the aerosol 108 is particularly important for commercial applications to increase the yield of  
10 high quality particulate product 116.

Often times it is desirable to use both the aerosol concentrator 236 and the droplet classifier 280 to produce an extremely high quality aerosol stream for introduction into the furnace for the production of particles of highly controlled size and size distribution. Referring now to Fig. 30, one embodiment of the present invention is shown incorporating  
15 both the virtual impactor 246 and the impactor 288. Basic components of the virtual impactor 246 and the impactor 288, as shown in Fig. 30, are substantially as previously described with reference to Figs. 16-29. As seen in Fig. 30, the aerosol 108 from the aerosol generator 106 is fed to the virtual impactor 246 where the aerosol stream is concentrated to produce the concentrated aerosol 240. The concentrated aerosol 240 is then fed to the  
20 impactor 288 to remove large droplets therefrom and produce the classified aerosol 282, which may then be fed to the furnace 210. Alternatively, the order of the aerosol concentrator and the aerosol classifier could be reversed, so that the aerosol concentrator 236 follows the aerosol classifier 280.

One important feature of the design shown in Fig. 30 is the incorporation of drains  
25 310, 312, 314, 316 and 296 at strategic locations. These drains are extremely important for industrial-scale particle production because buildup of liquid in the process equipment can

significantly impair the quality of the particulate product 116 that is produced. In that regard, drain 310 drains liquid away from the inlet side of the first plate assembly 248 of the virtual impactor 246. Drain 312 drains liquid away from the inside of the concentrating chamber 262 in the virtual impactor 246 and drain 314 removes liquid that deposits out of the excess carrier gas 238. Drain 316 removes liquid from the vicinity of the inlet side of the flow control plate 290 of the impactor, while the drain 296 removes liquid from the vicinity of the impactor plate 302. Without these drains 310, 312, 314, 316 and 296, the operation of the apparatus shown in Fig. 30 would not be satisfactory. All liquids drained in the drains 310, 312, 314, 316 and 296 may advantageously be recycled for use to prepare the liquid feed

10 102.

With some applications of the process of the present invention, it may be possible to collect the particles 112 directly from the output of the furnace 110. More often, however, it will be desirable to cool the particles 112 exiting the furnace prior to collection of the particles 112 in the particle collector 114. Referring now to Fig. 31, one embodiment of the process of the present invention is shown in which the particles 112 exiting the furnace 110 are sent to a particle cooler 320 to produce a cooled particle stream 322, which is then feed to the particle collector 114. Although the particle cooler 320 may be any cooling apparatus capable of cooling the particles 112 to the desired temperature for introduction into the particle collector 114, traditional heat exchanger designs are not preferred. This is because a traditional heat exchanger design ordinarily subjects the stream in which the particles 112 are suspended to cool surfaces. In that situation, significant losses of particles 112 occur due to thermophoretic deposition of the hot particles 112 on the cool surfaces of the heat exchanger. According to the present invention, a gas quench apparatus is provided for use as the particle cooler 320 that significantly reduces thermophoretic losses compared to a traditional heat exchanger.

20  
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Referring now to Figs. 32-34, one embodiment of a gas quench cooler 330 is shown.

The gas quench cooler includes a perforated conduit 332 housed inside of a cooler housing 334 with an annular space 336 located between the cooler housing 334 and the perforated conduit 332. In fluid communication with the annular space 336 is a quench gas inlet box 338, inside of which is disposed a portion of an aerosol inlet conduit 340. The perforated  
5 conduit 332 extends between the aerosol inlet conduit 340 and an aerosol outlet conduit 342. Attached to an opening into the quench gas inlet box 338 are two quench gas feed tubes 344. Referring specifically to Fig. 34, the perforated tube 332 is shown. The perforated tube 332 has a plurality of openings 345. The openings 345, when the perforated conduit 332 is assembled into the gas quench cooler 330, permits the flow of quench gas 346 from the  
10 annular space 336 into the interior space 348 of the perforated conduit 332.

With continued reference to Figs. 32-34, operation of the gas quench cooler will now be described. During operation, the particles 112, carried by and dispersed in a gas stream, enter the gas quench cooler 330 through the aerosol inlet conduit 340 and flow into the interior space 348 of perforated conduit 332. Quench gas 346 is introduced through the  
15 quench gas feed tubes 344 into the quench gas inlet box 338. Quench gas 346 entering the quench gas inlet box 338 encounters the outer surface of the aerosol inlet conduit 340, forcing the quench gas 346 to flow, in a spiraling manner, into the annular space 336, where the quench gas 346 flows through the openings 345 through the walls of the perforated conduit 332. In this manner, the quench gas 346 enters in a radial direction into the interior  
20 space 348 of the perforated conduit 332 around the entire periphery of the perforated conduit 332 and over the entire length of the perforated conduit 332. The cool quench gas 346 mixes with and cools the hot particles 212, which then exit through the aerosol outlet conduit 342 as the cooled particle stream 322. The cooled particle stream 322 can then be sent to the particle collector 114 for particle collection.

25 Because of the entry of quenched gas into the interior space 348 of the perforated conduit 322 in a radial direction about the entire periphery and length of the perforated

conduit 322, a buffer of the cool quench gas 346 is formed about the inner wall of the perforated conduit 332, thereby significantly inhibiting the loss of hot particles 112 due to thermophoretic deposition on the cool wall of the perforated conduit 332.

In an additional embodiment, the process of the present invention can also  
5 incorporate compositional modification of the particles 112 exiting the furnace. Most commonly, the compositional modification will be to coat the particles 112 with a coating material. One embodiment of the process of the present invention incorporating particle coating is shown in Fig. 35. As shown in Fig. 35, the particles 112 exiting from the furnace 110 go to a particle coater 350 where a coating is placed over the outer surface of the particles  
10 112 to form coated particles 352, which are then sent to the particle collector 114 for preparation of the particulate product 116.

In the particle coater, the particles 112 are coated using any suitable particle coating technology. Preferably, however, the coating is accomplished by chemical vapor deposition (CVD) or physical vapor deposition (PVD). In CVD coating, one or more vapor phase coating  
15 precursors are reacted to form a surface coating on the particles. In PVD coating, coating material, without chemical reaction, physically deposits on the surface of the particles 112. Another possible surface coating method is surface conversion of the surface portion of the particles 112 by reaction with a vapor phase reactant to convert a surface portion of the particles to a different material than that originally contained in the particles 112.

20 In a preferred embodiment, when the particles are coated according to the process of the present invention, the particles 112 are also manufactured via the aerosol process of the present invention, as previously described. The process of the present invention can, however, be used to coat particles that have been premanufactured by a different process, such as by a liquid precipitation route. When coating particles that have been  
25 premanufactured by a different route, such as liquid precipitation, it is preferred that the particles remain in a dispersed state from the time of manufacture to the time that the

particles are introduced in slurry form into the aerosol generator 106 for preparation of the aerosol 108 to form the dry particles 112 in the furnace 110, which particles 112 can then be coated in the particle coater 350. Maintaining particles in a dispersed state from manufacture through coating avoids problems associated with agglomeration and  
5 redispersion of particles if particles must be redispersed in the liquid feed 102 for feed to the aerosol generator 106. For example, for particles originally precipitated from a liquid medium, the liquid medium containing the suspended precipitated particles could be used to form the liquid feed 102 to the aerosol generator 106. It should be noted that the particle coats could be an integral extension of the furnace 110 as could be a separate piece of  
10 equipment.

In a further embodiment of the present invention, following preparation of particles 112 in the furnace 110, the particles may be structurally modified to impart desired physical properties prior to particle collection. Referring now to Fig. 36, one embodiment of the process of the present invention is shown including such structural particle modification.  
15 The particles 112 exiting the furnace 110 go to a particle modifier 360 where the particles are structurally modified to form modified particles 362, which are then sent to the particle collector 114 for preparation of the particulate product 116. The particle modifier 360 is typically a furnace, such as an annealing furnace, which may be integral with the furnace 110 or may be a separate heating device. Regardless, it is important that the particle modifier  
20 360 have temperature control that is independent of the furnace 110, so that the proper conditions for particle modification may be provided separate from conditions required of the furnace 110 to prepare the particles 112. The particle modifier 360, therefore, typically provides a temperature controlled environment and necessary residence time to effect the desired structural modification of the particles 112.

25 The structural modification that occurs in the particle modifier may be any modification to the crystalline structure or morphology of the particles 112. For example,



the particles 112 may be annealed in the particle modifier to densify the particles 112 or to recrystallize the particles 112 into a polycrystalline or single crystalline form. Also, especially in the case of composite particles 112, the particles may be annealed for a sufficient time to permit redistribution within the particles 112 of different material phases.

5        The initial morphology of composite particles made in the furnace 110 according to the present invention could take a variety of forms, depending upon the specified materials involved and the specific processing conditions. Examples of possibly composite particles morphologies are shown in Fig. 37. These morphologies could be those initially produced in the furnace 110 or that result from structural modification in the particle modifier 360.

10        While various specific embodiments of the process of the present invention and the apparatus of the present invention have been described in detail, it should be recognized that the features described with respect to each embodiment may be combined, in any combination, with features described in any other embodiment, to the extent that the features are compatible. For example, any or all of the aerosol concentrator, aerosol  
15 classifier, particle cooler, particle coater and particle modifier may be incorporated into the apparatus and/or process of the present invention. Also, additional apparatus and/or process steps may be incorporated to the extent they do not substantially interfere with operation of the process of the present invention or the apparatus useful therefore. For example, to further control the size distribution of particles produced accordingly to the process of the  
20 present invention, a particle classifier could be used after particle cooling and before particle collection. Other modifications will become apparent to those skilled in the art. All such modifications are intended to be within the scope of the present invention.

Referring now to Fig. 38, an embodiment of the apparatus of the present invention is shown that includes the aerosol generator 102 (in the form of the 400 transducer array  
25 design) the aerosol concentrator 236 (in the form of a virtual impactor), a droplet classifier 280 (in the form of an impactor), the furnace 110, the particle cooler 320 (in the form of a gas

quench cooler) and the particle collector 114 (in the form of a bag filter). All process equipment components are connected via appropriate flow conduits that are substantially free of sharp edges that could detrimentally cause liquid accumulations in the apparatus. Also, it should be noted that flex connectors 370 are used upstream and downstream of the aerosol concentrator 236 and the droplet classifier 280. By using the flex connectors 370, it is possible to vary the angle of slant of vertically extending slits in the aerosol concentrator 236 and/or the droplet classifier 280. In this way, a desired slant for the vertically extending slits may be set to optimize the draining characteristics off of the vertically extending slits for any particular particle manufacture operation in which the apparatus is to be used.

10 The aerosol generator of the present invention may have a different design depending upon the specific application. For example, when larger particles are desired, such as those above a size of about 8-10 microns, a spray nozzle atomizer may be used. For smaller-particle applications, however, and particularly for those applications to produce particles smaller than about 5 microns, an ultrasonic generator, as described herein, is preferred.

15 Although ultrasonic aerosol generators have been used for medical applications and home humidifiers, use of ultrasonic generators for spray pyrolysis particle manufacture has been largely confined to small-scale experimental situations.

The ultrasonic aerosol generator of the present invention described with reference to figures 2-15, however, is suited for commercial applications, and especially those in which extremely high quality particles of a narrow sized distribution are desired for speciality applications. In that regard, the aerosol generator produces a high quality aerosol, with heavy droplet loading and at a high rate of production. Such a combination of narrow size distribution, heavy droplet loading, and high production rate provide significant advantages over existing aerosol generators that usually suffer from at least one of inadequately narrow sized distribution, undesirably low droplet loading, or unacceptably low production rate.

Through the careful and controlled design of the ultrasonic generator of the present invention, an aerosol having greater than about 80 weight percent of droplets in the size range of from one micron to about 10 microns may be produced. Also, the ultrasonic generator of the present invention is capable of delivering high output rates of liquid feed  
5 in the aerosol. The rate of liquid feed, at the liquid loadings previously described, is preferably greater than about 25 milliliters per hour per transducer, more preferably greater than about 37.5 milliliters per hour per transducer, even more preferably greater than about 50 milliliters per hour per transducer and most preferably greater than about 100 milliliters per hour per transducer. This high performance is required for commercial applications and  
10 is accomplished with the present invention with a relatively simple design including a single precursor bath over an array of ultrasonic transducers. For example, when the aerosol generator has a 400 transducer design, as described with reference to Figures 5-15, the aerosol generator is capable of producing a high quality aerosol having high droplet loading as previously described, and a total production rate of preferably greater than about 10 liters  
15 per hour of liquid feed, more preferably greater than about 15 liters per hour of liquid feed, even more preferably greater than about 20 liters per hour of liquid feed and most preferably greater than about 40 liters per hour of liquid feed.

The present invention is particularly applicable to virtually any type of phosphor and examples of particular phosphors are detailed below. Phosphors are materials which are  
20 capable of emitting radiation in the visible or ultraviolet spectrum upon excitation, such as excitation by an external electric field. Phosphors can be chemically tailored to emit specific wavelengths of visible light, such as red, blue or green light. By dispersing various phosphor powders in a predetermined arrangement and controllably exciting the powders, a full-color visual display can be achieved.

25 Phosphors can be classified by their phosphorescent properties and the present invention is applicable to all types of these phosphors. For example, electroluminescent

phosphors are phosphors that emit light upon stimulation by an electric field. These phosphors are used for thin-film and thick-film electroluminescent displays, back lighting for LCD's and electroluminescent lamps used in wrist watches and the like. Cathodoluminescent phosphors emit light upon stimulation by electron bombardment. These materials are  
5 utilized in CRT's (e.g. common televisions) and FED's.

Photoluminescent phosphors emit light upon stimulation by other light. The stimulating light usually has higher energy than the emitted light. For example, a photoluminescent phosphor can emit visible light when stimulated by ultraviolet light. These phosphors are utilized in plasma display panels and common lamps.

10 Up-converter phosphors also emit light upon stimulation by other light, but usually light of a lower energy than the emitted light. For example, infrared light can be used to stimulate an up-converter phosphor which then emits visible light. Up-converter phosphors typically include at least 2 dopants which convert the lower energy infrared light to visible light. These materials are useful in immunoassay and security applications. Similarly, x-ray  
15 phosphors are utilized to convert x-rays to visible light and are useful in medical diagnostics.

Phosphors typically include a matrix compound, often referred to as a host material, and the phosphor further include one or more dopants, often referred to as an activator ion, to emit a specific color or to enhance the luminescence characteristics. Some phosphors, such as up-converter phosphors, will utilize more than one activator ion. Phosphor  
20 compounds used as host materials can include, but are not limited to, sulfides, oxides, borates, phosphates, halides, fluorides, silicates, oxysulfides and thiogallates. The host material is doped with from about 0.001 to about 5 weight percent, typically from about 0.02 to about 0.5 weight percent, of an activator ion.

Particular phosphor compounds may be preferred for certain applications and no  
25 single phosphor compound is necessarily preferred for all possible applications. However, preferred phosphor host materials for some display applications include the Group II sulfides

(e.g. CaS, SrS, BaS,  $Mg_xSr_{1-x}S$  and  $Ca_xSr_{1-x}S$ ) and the Group XII sulfides (e.g. ZnS, CdS and  $Zn_xCd_{1-x}S$ ).

Among these, ZnS is particularly preferred for many display applications, particularly those utilizing high voltages (i.e. greater than about 2000 volts), due primarily to the high brightness of ZnS. ZnS is typically doped with Cu, Ag, Al, Au, Cl or mixtures thereof. For

5 example,  $ZnS:Ag^{+1}$  is a common phosphor used to produce blue light in a CRT device.

Among the oxides,  $Y_2O_3$  doped with  $Eu^{3+}$  ( $Y_2O_3:Eu^{3+}$ ) is often preferred for emitting red light.  $BaMgAl_{11}O_{17}:Eu^{2+}$  (BAM: $Eu^{2+}$ ) is also a common oxide for producing blue light. Other compounds that would be useful if available include  $SrGa_2S_4:Eu^{3+}$ ,  $SrGa_2S_4:Ce^{3+}$ ,  $CaGa_2S_4:Eu^{3+}$  and  $CaGa_2S_4:Ce^{3+}$ . Preferred phosphor host materials and activators for particular

10 applications are discussed in more detail hereinbelow.

TABLE I Examples of Phosphor Materials

Host Material	Activator Ion	Color
BaS	Ce	Yellow
CaS	Ce	Green
15 CaS	Mn	Yellow
SrS	Ce	Blue-Green
$Mg_xSr_{1-x}S$	Ce	Blue-Green
ZnS	Cu	Blue-Green
BAM	Eu	Blue
20 ZnO	Zn	Green
$Y_2O_3$	Eu	Red
$(Ce,Gd)MgB_5O_{10}$	Tb	Green
$Y_2O_2S$	Eu	Red

25 The powder characteristics that are preferred will depend upon the application of the phosphor powders. Nonetheless, it can be generally stated that the powders should usually have a small particle size, narrow size distribution, spherical morphology, high density/low

porosity, high crystallinity and homogenous dopant distribution. The efficiency of the phosphor, defined as the overall conversion of excitation energy to visible photons, should be high.

According to the present invention, the phosphor powder consists of particles having  
5 a small size. Although the preferred size of the phosphor particles will vary according to the application of the phosphor powder, the average particle size of the phosphor particles is preferably less than about 10  $\mu\text{m}$ . For most applications, the average particle size is more preferably from about 0.1  $\mu\text{m}$  to about 5  $\mu\text{m}$  and even more preferably is from about 0.5  $\mu\text{m}$  to about 2  $\mu\text{m}$ .

10 According to the present invention, the powder batch of phosphor particles also has a narrow particle size distribution, such that the majority of particles are substantially the same size. Preferably, at least about 90 percent of the particles by number and more preferably at least about 95 percent of the particles by number are smaller than twice the average particle size. Thus, when the average particle size is about 2  $\mu\text{m}$ , it is preferred that  
15 at least about 90 percent of the particles are less than 4  $\mu\text{m}$  and it is more preferred that at least about 95 percent of the particles are less than 4  $\mu\text{m}$ . Further, it is preferred that at least about 90 percent of the particles by number are less than about 1.5 times the average particle size. Thus, when the average particle size is about 2  $\mu\text{m}$ , it is preferred that at least about 90 percent of the particles are less than 3  $\mu\text{m}$ .

20 The phosphor particles of the present invention can be substantially single crystal particles or may be comprised of a number of crystallites. It is possible according to the present invention to produce phosphor particles having large crystallites. Crystallite size can be determined from the width of the x-ray diffraction peaks of the material. Large crystallites give rise to sharp peaks, while the peak width increases as crystallite size  
25 decreases.

It is preferred that the average crystallite size within the particles is at least about 50

nanometers and more preferably is at least about 100 nanometers. The average crystallite size most preferably approaches the average particle size such that the particles are mostly single crystals. Preferably, the average crystallite size is at least about 50 percent and more preferably at least about 80 percent of the average particle size. Highly crystalline phosphors  
5 (i.e. large crystallite size) are believed to have increased efficiency as compared to phosphors with smaller crystallites.

The phosphor particles of the present invention advantageously have a high degree of purity, that is, a low level of impurities. Impurities are those materials that are not intended in the final product -- thus, an activator ion is not considered an impurity. The level  
10 of impurities in the phosphor powders of the present invention is preferably less than about 0.1 weight percent and is more preferably less than about 0.01 weight percent. Further, the activator ion is homogeneously dispersed throughout the host material.

The phosphor particles are also very dense and preferably have a powder density of at least about 80 percent of the theoretical density, more preferably at least about 90  
15 percent of the theoretical density and even more preferably at least about 95 percent of the theoretical density.

The particles of the present invention are also substantially spherical in shape. Spherical particles are particularly advantageous because they are able to disperse and coat a device more uniformly. As a result, the phosphor powder batch of the present invention  
20 is substantially non-agglomerated and has good dispersibility in a variety of media.

As is discussed above, it is often advantageous to provide phosphor particles with a coating on the outer surface thereof. Coatings are often desirable to reduce degradation of the phosphor material due to moisture or other influences such as the plasma in a plasma display device or electron bombardment in cathodoluminescent devices. For example, metal  
25 sulfides such as ZnS are particularly susceptible to degradation due to moisture and should be completely encapsulated to reduce or eliminate the degradation reaction. Other

phosphors are known to degrade in an electron beam operating at a high current density, such as in field emission displays and CRT's.

Preferred coatings include metal oxides such as  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$  or  $\text{In}_2\text{O}_3$ . Semiconductive oxide coatings such as  $\text{SnO}$  or  $\text{In}_2\text{O}_3$  can advantageously absorb secondary  
5 electrons that are often emitted by the phosphor. The coatings can be either particulate coatings or non-particulate (film) coatings. The coatings should be relatively thin and uniform. Preferably, the coating has an average thickness of less than about  $1\text{ }\mu\text{m}$  and more preferably the average coating thickness is from about 5 nanometers to about 100 nanometers. Further, the particles can include more than one coating substantially  
10 encapsulating the particles to achieve the desired properties.

In addition, the phosphor particles can include organic coatings such as PMMA (polymethylmethacrylate), polystyrene or the like. The organic coating should be on the order of 1 to 100 nanometers thick and be substantially dense and continuous about particle. Such coatings can be formed after the powders are prepared by a liquid phase process. The  
15 organic coatings can advantageously prevent corrosion of the phosphor particles especially in electroluminescent lamps and also can improve the dispersion characteristics of the particles.

The coating can also be a monolayer coating formed by the reaction of an organic or an inorganic molecule with the surface of the phosphor particles to form a coating that is  
20 essentially one molecular layer thick. In particular, the formation of a monolayer coating by reaction of the surface of the phosphor powder with a functionalized organo silane such as halo- or amino-silanes, for example hexamethyldisilazane or trimethylsilylchloride, can be used to modify/control the hydrophobicity and hydrophilicity of the phosphor powders. Such coatings allow for greater control over the dispersion characteristics of the phosphor  
25 powder in a wide variety of paste compositions.

The monolayer coatings may also be applied to phosphor powders that have already

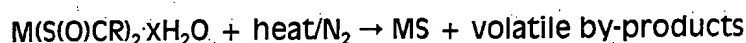
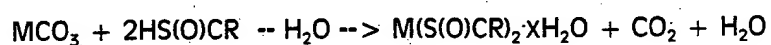


been coated with, for example, 1-100 nanometer organic or inorganic coatings thus providing better control over the corrosion characteristics (through the use of thicker coating) as well as dispersibility (through the monolayer coating) of the phosphor powder.

The phosphor powders of the present invention are preferably produced using a spray pyrolysis method. The method generally includes the steps of providing a solution of a phosphor particle precursor, forming droplets from the solution (an aerosol), moving the droplets in a carrier gas, classifying the droplets to remove droplets larger than a specified size, and passing the droplets through a heating zone to evaporate the solvent and sufficiently heat the precursor materials to form the desired phosphor particles.

10 The precursor solution includes the chemical components that will form the phosphor particles, including the activator ions. The solution can contain nitrates, carbonates or the like. For example, the nitrates can be used as the precursor materials for both an yttria host material and a europium activator ion.

More specifically, doped metal sulfide phosphors (MS:M') can be prepared from an aqueous solution by the reaction of a metal carbonate (or oxide or hydroxide) with a sulfur-containing acid such as thioacetic acid or thiocarboxylic acid (HS(O)CR) forming a water soluble complex, such as  $M(S(O)CR)_2 \cdot xH_2O$  or from a soluble metal salt and sulfur-containing ligand such as thiourea. Preferably, at least about 2 equivalents of acid are added to ensure complete reaction with the metal compound. The solution, when pyrolyzed under  $N_2$ , leads to the metal sulfide.



The solution preferably has a phosphor precursor concentration that is unsaturated to avoid the formation of precipitates and preferably includes from about 1 to about 50 weight percent of the precursor. Preferably the solvent is aqueous-based for ease of operation, although other solvents, such as toluene, may be desirable for specific materials.

The use of organic solvents can lead to undesirable carbon concentration in the phosphor particles. The pH of the aqueous-based solutions can be adjusted to alter the solubility characteristics of the precursor in the solution.

The precursor solution is formed into a plurality of droplets, i.e. an aerosol, using a droplet generator. For example, an aerosol can be formed by nozzles or other types of atomizers. The solution is preferably formed into droplets using an ultrasonic nebulizer wherein ultrasonic transducers are disposed in relation to the solution such that the vibrational energy of the transducers can be efficiently translated to the solution, although it is not necessary that the transducers be in direct contact with the solution. It may be preferable to utilize a barrier between the transducer and the solution, particularly when the solution has a tendency to degrade the transducer material. To prevent such adverse conditions, the transducers can be placed in distilled water which transfers the vibrational energy to a membrane separating the water and the precursor solution.

The transducers preferably vibrate at a frequency of from about 1 MHz to about 5 MHz, more preferably from about 1.5 MHz to about 3MHz, most preferably from about 1.6 to about 2.4 MHz. The average size of the droplets produced is dependent upon a number of factors, including the density of the solution, the concentration of precursor material in the solution and the frequency of the generator. Generally, the average size of the droplets decreases with increasing vibrational frequency. According to one embodiment of the present invention, the droplets have an average size of from about 1  $\mu\text{m}$  to about 10  $\mu\text{m}$ , more preferably from about 1  $\mu\text{m}$  to about 5  $\mu\text{m}$ .

A carrier gas under controlled pressure is introduced to the aerosol generator to move the droplets away from the generator. The carrier gas can be an inert carrier gas or an active carrier gas that is capable of reacting with the precursor or other available materials to affect the bulk composition of the particle or to coat the particles. Examples of preferred carrier gases include reactive carrier gases such as air or oxygen and inert carrier

gases such as argon or nitrogen.

As the droplets are formed and carried away by the carrier gas, the solution will begin to concentrate over time. Therefore, the precursor solution is constantly recirculated to maintain a substantially constant concentration of precursor material. If the concentration  
5 of the precursor increases too greatly, the average droplet size can increase to an undesirable level.

The carrier gas is adapted to move the droplets in aerosol form to a heating zone where the droplets are heated to react and form solid particles. According to a preferred embodiment of the present invention, the droplets are classified prior to entering the  
10 heating zone to remove droplets having a size greater than a maximum size. For example, droplets having a size greater than about 3 times the average droplet size are removed and more preferably droplets having a size greater than 2 times the average droplet size are removed. In one embodiment, droplets having a size greater than about 10  $\mu\text{m}$  are removed.

15 Droplets having a size greater than a preselected maximum size can be removed from the droplet stream using a number of methods, including a cyclone. In a preferred embodiment, the larger droplets are removed using an impactor. An impactor is a device which utilizes inertia to remove large particles from the flow stream. An inertial impactor utilizes a wall that is situated in the path of the flowing carrier gas. The wall has a gap or hole  
20 at an end that is spaced from the center of the wall. Small particles, with lower inertia, flow with the carrier gas through the gap. Larger particles impact upon the wall and are thereby removed from the carrier gas stream. The larger particles, now in the form of a liquid stream, flow down the impactor wall and the resultant solution can advantageously be recycled. The maximum particle size can be adjusted by adjusting the various dimensions  
25 of the impactor.

In addition to removing maximum size droplets, it can also be advantageous to

remove minimum size droplets from the carrier gas stream. Preferably, minimum size droplets are removed from the carrier gas stream using a virtual impactor. A virtual impactor also uses inertial forces to separate the droplets. The carrier gas stream enters the virtual impactor and is passed through a first aperture. Opposite the first aperture is a  
5 second aperture located directly across from the first aperture. The carrier gas is removed from the virtual impactor in a direction substantially perpendicular to the flow of the carrier gas. Thus, a majority of the gas from the carrier gas stream is removed and the removed gas carries with it all droplets having insufficient inertia, i.e. small enough size, to be carried out of the path of the second aperture. Droplets above a minimum size continue in a  
10 substantially straight path through the second aperture.

In a preferred embodiment, droplets having a size smaller than about  $1/3$  the average size of the droplets are removed and in a more preferred embodiment droplets having a size smaller than about  $1/2$  the average size are removed from the aerosol.

In addition to removing smaller droplets and thereby narrowing the size distribution  
15 of droplets, the virtual impactor advantageously removes a majority of the carrier gas thereby concentrating the droplets in the carrier gas stream. Thus, the mass of droplets per volume of carrier gas can advantageously be increased which advantageously increases the production rate of the particles.

The carrier gas stream containing the classified precursor droplets is then transported  
20 to a heating zone. The heating zone is adapted to heat the droplets to a sufficient temperature for a sufficient time to evaporate the solvent and react the particle precursor to form solid particles therefrom. Preferably, the heating zone includes an elongated ceramic tube that is heated to form hot zone within the tube. The heating can be achieved by any means known in the art, such as electrical resistance heating or the like. The heating  
25 zone has a sufficient volume such that significant particle interaction is avoided. The total residence time in the heating zone can be up to about 100 seconds and is preferably from

about 0.1 seconds to about 10 seconds, more preferably from about 0.5 to about 2 seconds. The peak temperature of the heating zone is preferably from about 500°C to about 1800°C, depending upon the phosphor that is being produced.

The reacted particles exit the heating zone and are separated from the carrier gas.

5 Thermophoretic losses are preferably avoided at the outlet of the heating zone. Thermophoretic losses are caused by the attraction of the hot particles exiting the heating zone to the cold walls of the outlet. The particles are preferably quenched in a cooling gas that is radially circulated at the outlet of the heating zone. Preferably, a filter is used to separate the particles from the carrier gas and the particles are collected.

10 While powders produced by the foregoing method have good crystallinity, it may be desirable to increase the crystallinity after production. Thus, the powders can be heated for varying amounts of time and in different environments to increase the crystallinity of the phosphor. Increased crystallinity will lead to a increase brightness and efficiency of the phosphor. If such annealing steps are performed, the annealing temperature and time  
15 should be selected to minimize the amount of interparticle sintering that is often associated with annealing. For example, yttria-based phosphors annealed at 1400°C under air for 58 hours can advantageously increase in brightness intensity by 160 percent or more due to an increase in the crystallite size.

Further, the crystallinity of the phosphors can be increased by using a fluxing agent,  
20 either in the precursor solution or in a post-formation annealing step. A fluxing agent is a reagent which improves the crystallinity of the material when the reagent and the material are heated together as compared to heating the material to the same temperature and for the same amount of time in the absence of the fluxing agent. The fluxing agent, for example alkali metal halides such as NaCl or KCl, can be added to the precursor solution  
25 where it improves the crystallinity of the particles during their subsequent formation. Alternatively, the fluxing agent can be added to the phosphor powder batches after they

have been collected. Upon annealing, the fluxing agent improves the crystallinity of the phosphor powder, and therefore improves the brightness of the phosphor powder.

By applying the foregoing methodology, very good production rates of phosphor powders can be achieved. For example, particles having a size of from about 1 to about 5  $\mu\text{m}$  can be produced at a rate of greater than about 250 g/hr, such as from about 500 to about 1000 g/hr. Further, the particles have a very spherical morphology, which can be advantageous for many applications.

As is discussed above, it may be desirable to form phosphor particles with coatings thereon to enhance the stability or other properties of the phosphor powders. The phosphor powders of the present invention can be coated using several different methods. For example, a colloidal phosphor powder and a soluble, involatile molecular precursor to the coating can be suspended in the droplets so that the coating forms around the phosphor when passed through the heating zone. Alternatively, a soluble precursor to both the phosphor powder and the coating can be used in the precursor solution wherein the coating precursor is involatile (e.g.  $\text{Al}(\text{NO}_3)_3$ ) or volatile (e.g.  $\text{Sn}(\text{OAc})_4$ ). In another method, a colloidal precursor and a soluble phosphor precursor can be used to form a particulate colloidal coating on the phosphor.

In yet another coating method, a volatile coating precursor or precursor solution is sprayed into the spray pyrolysis reactor at a point where the phosphor particles have already been formed. The precursor reacts to form a coating on the phosphor particle surface. These coatings can be generated by two different mechanisms. First, the precursor can vaporize and diffuse to the hot particle surface and thermally react resulting in the formation of a thin-film by chemical vapor deposition (CVD). Alternatively, the gaseous precursor can react in the gas phase forming small particles (e.g. less than about 5 nanometers) which can then diffuse to the particle surface and sinter onto the surface forming a coating. This reaction mechanism is referred to as gas to particle conversion (GPC).

In addition, a volatile coating material, such as  $\text{PbO}$ ,  $\text{MoO}_3$  or  $\text{V}_2\text{O}_5$ , can be introduced into the reactor such that the coating deposits on the particle by condensation.

5 An additional heating zone, such as a second elongated tubular furnace, can be added after the main reactor but before the quench system, coat the particles with the desired coating.

The phosphor powders of the present invention are useful in a number of applications and the present invention includes intermediate products, for example pastes, and also includes novel devices that are constructed using the phosphor powders. Such  
10 devices include, but are not limited to, CRT-based devices such as televisions, liquid crystal displays, plasma displays, (PDP's) thin and thick film electroluminescence displays, field emissive displays (FED'S), electroluminescent lamps, and high definition televisions (HDTV's).

The high electron voltages and small currents required to activate the phosphors efficiently have caused problems in the wide spread development of flat panel displays.  
15 Phosphors for flat panel displays must operate at a lower voltage and higher current density and efficiency than phosphor materials used in existing cathode ray tubes. The low voltages used in most flat panel displays result in an electron penetration depth in the range of several micrometers down to tens of nanometers, depending on the voltage. Thus, the control of size and crystallinity is important. If large agglomerated powders are used, only  
20 a fraction of the exudation electrons will interact with the phosphor. Use of phosphor powders having a wide size distribution can also lead to non-uniform pixels and sub-pixels which leads to a blurred image.

Plasma displays are useful for large display applications since very large display screens can be formed without loss of performance. In a plasma display, a gas is placed between  
25 two electrodes and a high energy electric field is generated between the electrodes. Upon reaching a critical voltage a plasma is formed and light is emitted. A plasma display includes

a thin-film dielectric layer which provides high secondary electron emissions to improve the efficiency and performance of the display. Preferred photoluminescent phosphors for use in plasma displays are  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  for displaying green light,  $(\text{Y,Gd})\text{BO}_3\text{:Eu}$  for displaying red light and  $\text{BaMgAl}_{14}\text{O}_{23}\text{:Eu}$  for displaying blue light.

- 5           Field emissive displays (FED's) advantageously eliminate the size, weight and power consumption problems of CRT's and are useful for portable electronics, such as laptop computers. FED's generate electrons from millions of cold microtip emitters with low power emission. These emitters are arranged in a large matrix addressed array with several emitters allocated to each pixel in the display. The microtip emitters are located approximately 0.2
- 10 millimeter from a cathodoluminescent phosphor screen which generates the display image. This allows for thin, light-weight packaging. FED's require low-voltage phosphor materials, that is, phosphors which emit sufficient light under low applied voltages, such as less than about 500 volts. Many phosphor materials such as ZnS and CdS suffer from breakdown due to the high electron beam current density used in FED display configurations. For this
- 15 reason, preferred materials for use in FED's include  $\text{ZnO:Zn}$  for green light,  $\text{SrGa}_2\text{S}_4\text{:Eu}$  for green light,  $\text{Y}_2\text{O}_3\text{:Eu}$  for red light, and  $\text{Y}_2\text{SiO}_5\text{:Ce}$  or  $\text{ZnS:(Ag, Al or Cl)}$  for blue light.

Electroluminescent lamps are formed on flexible polymer substrates and are used as back lights for cellular phones, watches, personal digital assistants and the like. A phosphor powder/polymer composite is sandwiched between two electrodes, the front electrode

20 being transparent. Preferred electroluminescent phosphors for use in these devices include  $\text{ZnS:Cu}$  for blue-green,  $\text{BaS:RE}$  or  $\text{Mn}$ ,  $\text{CaS:RE}$  or  $\text{Mn}$ ,  $\text{SrS:RE}$  or  $\text{Mn}$ ,  $\text{Sr}_x\text{Ca}_y\text{Ba}_{1-x-y}\text{S:RE}$ ,  $\text{ZnS:Mn}$  (where RE is a rare earth element) for other colors.

Preferred cathodoluminescent phosphors for CRT's include  $\text{ZnS:Cu}$  for green light,  $\text{ZnS:Ag,Au,Cl}$  for blue light and  $\text{Y}_2\text{O}_2\text{S:Eu}$  for red light.

- 25           Electroluminiscent displays also work by electroluminiscence. Such displays can be monochromatic or full color and typically use thin-film phosphors. However, powder



phosphors such as those disclosed herein are becoming increasingly more important for such displays. These displays can be produced at very small screen sizes without loss of resolution and are typically used in military applications as well as medical applications or any application where small screen display is desired.

5        Phosphors according to the present invention can also be used in common lighting. Such phosphors work by photoluminescence and mixtures of phosphors are used to produce white emitting light. Phosphors are applied to the inside of the glass lamp with trapped mercury vapor which generates ultraviolet light and thereby excites the phosphors to emit visible light.

10       Phosphors are also used as taggents for security purposes. In this application, up-converter phosphors, which are undetectable under normal lighting, become visible upon illumination by a particular energy, typically infrared radiation, emitting characteristic colors. Such taggents can be applied to explosives, currency or any other item that may require coding. Useful phosphors for taggent applications include  $\text{SrS:Sm}$ ,  $\text{Eu}$  and  $\text{YF}_3\text{:Er,Yb}$ , both of  
15 which emit visible light upon excitation.

Up-converter phosphors are also useful in immunoassay applications. Immunoassays are bioactive agent detectors designed to detect chemicals in the bloodstream, such as sugars, insulin or narcotics. The phosphor is delivered to the biological substrate and the interaction between the substrate and the underlying phosphor results in a detected color  
20 shift which can be correlated with the concentration of the initial bioactive molecule present in the sample. The up-converter phosphors of the present invention preferably have a particle size of from about 0.1 to about 0.4  $\mu\text{m}$  and are preferably coated to bind the biologically active molecule. Preferred phosphors include  $\text{SrS:Sm}$ ,  $\text{Eu}$  and  $\text{YF}_3\text{:Er,Yb}$ , as well as other oxide and oxysulfide host materials.

25       For many of the foregoing applications, phosphor powders are often dispersed within a paste which is then applied to a surface to obtain a phosphorescent layer. These pastes are

commonly used for electroluminescent lamps, FED's, plasma displays, CRT's, lamp phosphors and thick-film electroluminescent displays. The powders of the present invention offer many advantages when dispersed in such a paste. For example, the powders will disperse better than non-spherical powders of wide size distribution and can therefore produce thinner and  
5 more uniform layers and a brighter display. The packing density of the phosphors will also be higher. The number of processing steps can also be advantageously reduced. For example, in the preparation of electroluminescent lamps, two dielectric layers are often needed to cover the phosphor paste layer because many of the phosphor particles will be large enough to protrude through one layer. Spherical particles that are substantially  
10 uniform in size will eliminate this problem and the EL lamp will advantageously require one dielectric layer.

Phosphor paste compositions are disclosed in U.S. Patent No. 4,724,161, U.S. Patent No. 4,806,389, U.S. Patent No. 4,902,567 which are incorporated herein by reference in their entirety. Generally, phosphors are deaggregated and are combined with organic additives  
15 to form the paste.

### EXAMPLES

In order to demonstrate the advantages of the present invention, the following examples were prepared.

#### 1. **SrS:Mn<sup>2+</sup>**

20 1 gram of strontium carbonate (SrCO<sub>3</sub>) was added to 20 mL of deionized water. The suspension was stirred and about 1 mL of thioacetic acid and 0.003 grams MnCl<sub>2</sub> were added. The strontium carbonate rapidly dissolved into solution to form a clear, pale-yellow solution.

The solution was placed in an ultrasonic nebulizer operating at a frequency of about 1.6 MHz to produce an aerosol of solution droplets. A carrier gas consisting of nitrogen was  
25 used to carry the droplets into an elongate tubular furnace heated to a temperature of 600-1500°C. The resulting powder was a substantially phase-pure SrS with Mn<sup>2+</sup> incorporated as

a dopant, a green phosphor commonly used in electroluminescent lamps. The average particle size was about  $1.0\ \mu\text{m}$ . X-ray diffraction indicated that the particles consisted of phase pure SrS with high crystallinity. --

The foregoing process chemistry utilizing metal carbonates and thioacetic acid was also used to produce MgS, BaS, CaS,  $\text{Ca}_x\text{Sr}_{1-x}\text{S}$  and  $\text{Mg}_x\text{Sr}_{1-x}\text{S}$  under similar reaction conditions, i.e., a reactor temperature of  $800\text{--}1100^\circ\text{C}$  under  $\text{N}_2$  gas. ZnS was similarly produced at a reaction temperature of  $800\text{--}950^\circ\text{C}$ .

## 2. $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$

10 Yttrium nitrate and europium nitrate were dissolved in distilled water to make a 5.2 weight percent  $\text{Y}_2\text{O}_3$  solution with 4 mole percent Eu per Y. The solution was atomized as in Example 1. The droplets were passed through an impactor to remove droplets having an aerodynamic diameter of greater than about  $10\ \mu\text{m}$ . The droplets were then passed through a heated reaction zone heated to a peak temperature of about  $1100^\circ\text{C}$ . The resulting powder had a spherical particle morphology with an average particle size of  $0.96\ \mu\text{m}$ . The particles were highly crystalline phase pure  $\text{Y}_2\text{O}_3$  as shown by x-ray diffraction and had a density of 99 percent of the theoretical density for  $\text{Y}_2\text{O}_3$ .

Similar runs were performed using yttrium chloride and yttrium acetate as the yttrium precursors. Both resulted in an observation of decreased density of the particles indicating that the nitrates are a preferred precursor for the production of dense particles.

20 While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations of those embodiments will occur to those skilled in the art. However, it is to be expressly understood that such modifications and adaptations are within the spirit and scope of the present invention.